

## A method for manufacturing paper and paper

The present invention relates to a method for manufacturing paper in accordance with the independent patent claims presented below. The invention also relates to paper.

Fillers containing mineral materials, such as natural fine-ground calcium carbonate, precipitated calcium carbonate (PCC), kaolin and talc are used in paper manufacture in order to improve various paper properties, including optical and printing properties. Furthermore, adding filler makes it possible to use a smaller amount of fibre material in paper manufacture. The cost savings thus achieved generally clearly exceed the costs of the filler added.

It is thus generally considered desirable to add as much filler as possible to the fibre suspension used in paper manufacture. Due to factors relating to the strength properties of the paper, however, the amount of filler added, such as calcium carbonate, may not usually exceed 20–25%.

In order to increase the amount of calcium carbonate, it has been proposed that a calcium-based filler be added to the fibre suspension in the form of calcium hydroxide, and that the calcium therein be converted into precipitated calcium carbonate by adding carbon dioxide gas. This will cause the calcium carbonate to precipitate and adhere both directly onto the surface and also into the fibres, and in this way more carbonate can be added to the paper.

Weaknesses of these prior art solutions may be considered to be that:

- the precipitation reactions require a relatively long time to take place,
- the precipitation reactions are partially incomplete,
- the processes used are not continuous, or
- the apparatuses used are not easily integrated into the paper manufacturing process.

U.S Pat. No. 6,471,825 suggests precipitating the calcium hydroxide added to the fibre suspension directly onto the fibres in calcium carbonate form. In this case it is proposed that the suspension containing fibres and calcium hydroxide be first treated in a disc refiner-type apparatus in order to disperse any fibre bundles prior to feeding the carbon dioxide gas into the suspension.

In disc refiner-type apparatuses the fibre suspension is exposed to rough treatment that has a weakening effect on the fibre material. After feeding the carbon dioxide into the fibre suspension, the suspension is mixed in an auger mixer. However, with conventional precipitation reactors equipped with blade or auger mixers it is difficult to ensure the fast and efficient mixing of the carbon dioxide and calcium hydroxide, thus securing as complete as possible a reaction. In these reactors it is also hard to achieve binding of the precipitated calcium carbonate to the fibres.

U.S Pat. No. 5,679,220, in turn, discloses a method wherein the calcium hydroxide added to the fibre suspension is precipitated onto the fibres in the form of calcium carbonate with the help of carbon dioxide gas, while the fibre suspension flows through a long, two-compartment, tube-like reactor with smooth interior walls. The suspension containing calcium hydroxide is fed into the fibre suspension at about the middle of the first compartment of the tube-like reactor. Carbon dioxide gas is fed into the fibre suspension both before and after feeding the suspension containing calcium hydroxide into it. The carbon dioxide gas is fed into the reactor through an inlet formed in the wall of the reactor with the purpose of causing the gas to be absorbed into the suspension flowing past inside the tube. The residence time of the fibre suspension in the relatively long mixing reactor, exceeding 2 meters in length, is more than 1 minute.

Furthermore, methods of paper manufacture are known wherein the fibre material is loaded with filler material, as is disclosed, for example, in the EP application 969141. It is characteristic of this method that the paper is calendered after the

web formation. The pretreatment of the fibre material, wherein the fibres are provided with calcium carbonate, is not disclosed in great detail in the publication.

Consequently, the aim of the present invention is to create a paper manufacturing method superior to previous methods. A further aim of the invention is to create a superior paper.

The purpose is to create a method wherein the above-mentioned problems of the prior art have been minimised.

The purpose is thus firstly to create a method for ensuring that the fibres and the mineral material, such as calcium hydroxide or calcium oxide, and the precipitant chemical, such as carbon dioxide gas, are very well mixed during the precipitation process, and to enable the manufacture of paper from fibre material pretreated in such a way.

The purpose is thus also to create a method that enables the precipitation of the calcium carbonate onto or into the fibres to start and occur in a very short time and as completely as possible.

The purpose is hereby also to create a method that enables the filler content of the paper to be increased compared to that achieved by conventional practices.

The purpose is also to create a method that enables the properties, typically the optical and strength properties of the paper, paperboard or other corresponding product, to be influenced in a desired manner.

The purpose is also to create a method suitable for use in precipitating mineral material onto the fibres of very different fibre suspensions and onto any other solid material present in the said fibre suspension.

A further purpose is to obtain a continuous process for manufacturing paper, paperboard or a corresponding product in web form.

In order to achieve the above-mentioned objectives, the method and the paper of the present invention are characterised by what is presented in the detailed description of the invention presented below in the independent patent claims.

The present invention relates to a method of paper manufacture, generally comprising the following steps:

- (a) the fibre material that is used as raw material for the paper pulp is fed into the precipitation reactor;
- (b) a reactive mineral material, such as calcium hydroxide  $\text{Ca}(\text{OH})_2$ , is fed into the precipitation reactor;
- (c) the reactive mineral material and the fibre material are combined to form a fibre suspension in the precipitation reactor and/or prior to feeding these materials into the precipitation reactor;
- (d) the fibre suspension is brought into contact with the precipitant of said reactive mineral material in the precipitation reactor, in order to precipitate the reactive mineral material within the suspension at least partially, whereby at least some of the thus formed precipitated mineral material is precipitated onto the fibres within the fibre suspension, in such a manner that (d1) gas containing a substance, such as carbon dioxide, that precipitates the said mineral material, is fed into the precipitation reactor in order to form a gas space containing said precipitant inside the precipitation reactor, and (d2) the fibre suspension fed into the precipitation reactor and/or formed therein is dispersed, or scattered, in the form of small particles, such as drops and/or particles containing solid matter and/or liquid, into said gas space;

(e) the fibre suspension treated in this manner is discharged from the precipitation reactor;

whereafter the paper pulp formed by the fibre suspension is fed onto the forming section of the paper machine and is made into paper by allowing the pulp to drain through a permeable forming base.

Typically a gaseous precipitant is fed in a continuous gas stream into the precipitation reactor in order to maintain the desired gas space inside the reactor. The amount of precipitant in the gas may be varied considerably, depending on, for example, the source of the gaseous precipitant, its quality, and/or the desired paper properties. The gas fed into the precipitation reactor usually contains a precipitant, such as carbon dioxide, >5%, typically >10%, even 100% if desired. The gas containing the precipitant may thus be pure or nearly pure carbon dioxide, flue gas or other suitable gas or gas mixture containing carbon dioxide. If desired, other precipitants than carbon dioxide suitable for precipitating the chosen reactive mineral material may naturally be used. The gas is typically fed into the precipitation reactor in such a manner that will create an over-pressure inside the precipitation reactor.

The method of the present invention aims at feeding the fibre suspension, with its liquid and solid phases, into the gas space dispersed into extremely small parts in the form of drops and/or particles. The fibre suspension is in this case dispersed, according to a known or new method, into pure liquid drops; liquid drops that contain solid matter, such as fibres and mineral material; solid matter particles and/or solid matter particles coated with liquid. The fibre material in the fibre suspension is thus dispersed, at least partly, into separate fibres. The liquid phase of the fibre suspension is dispersed on the other hand into liquid drops mainly <10 mm, typically < 1 mm. The small liquid drops, fibres and other solid matter particles disperse into the gas space to form an almost mist-like gas suspension, which has a volume flow rate considerably higher than that of the

fibre suspension being fed into the reactor. This creates a large contact area between the drops and/or particles and the surrounding gas, which enables extremely fast and complete precipitation reactions between the reactive mineral material to be precipitated and the precipitant in the gas.

When applying the method of the present invention, it may furthermore be assumed that, principally, nearly every separate fibre is surrounded by a gas envelope, which causes fast and efficient precipitation of the mineral material from the surrounding liquid onto the fibre surfaces and into the fibre. Previously the aim has been, conversely, to feed gas in fine bubbles into a more or less viscous fibre suspension, in which method the precipitation process is not as fast or as efficient as with the present invention.

In applying the method of the present invention, extremely active precipitated material areas are formed on the fibres, through which areas the fibres presumably form inter-fibre bonds while the precipitation reactions continue in these areas. These bonds enhance the strength properties of the manufactured paper.

According to a preferred embodiment of the invention an activation zone has been formed in front of or into the precipitation reactor, preferably at its starting point in relation to the flow of the fibre material. In the activation zone, the fibre suspension is exposed to forces that activate the fibres, for example, tribomechanically or tribochemically, in a way that enhances the capacity of the fibres to bond with each other or to bind precipitating and/or precipitated mineral material to themselves. Activating the fibres has a positive effect on the strength properties of the manufactured paper.

In the activation zone of the preferred embodiment, the fibre suspension may be both dispersed into small drops and/or particles and activated. This activation is

preferably carried out in alkaline conditions, while the fibres are swollen due, for example, to the addition of  $\text{Ca}(\text{OH})_2$ .

In the activation zone, the fibre suspension may be subjected, for example, to successive impacts, counter impacts, shearing forces, turbulence, over- and under-pressure pulses or corresponding forces that mechanically activate the fibres, particularly their surfaces, for example by fibrillating or grinding the fibres or opening the inner parts of the fibres (lumen) to the mineral material. On the other hand, fibres, especially fibre surfaces, may also be activated chemically in such a way that active OH-groups are formed on their surfaces.

According to a preferred embodiment of the invention, the activation may be induced, for example, in a precipitation reactor with an activation zone provided with a flow-through mixer operating by the so-called multi-cage impact mill principle, with several, typically 3–8, most typically 4–6 concentric cages equipped with blades or the like. At least every other one of the cages acts as a rotor and the adjacent cages act as stators or rotors moving in different directions or at different speeds. The speed of the rotors may vary between 5 and 250 m/s. The speed difference of adjacent cages is 10–500 m/s, typically 50–200 m/s. Mills or mixers operating by this principle have previously been presented, for example, in the Finnish patent publications 105669B, 105112B and in publication WO-96/18454.

In a flow-through mixer operating by the impact mill principle, the fibre suspension is typically passed through the mixer radially outwards from the cage centres, which enables the blades or the like on the cages to bring impacts and counter impacts to bear on the outward flowing fibre suspension, thus creating shearing forces, turbulence and under- and over-pressure pulses, which have a fibre-activating effect. A reactor operating by the impact mill principle can efficiently treat fibre suspensions with both high and with very low solid matter contents, making them suitable for the precipitation phase. In a precipitation reactor in accordance with the present invention, it is therefore possible to

precipitate mineral materials with highly varying solid matter contents, such as 0.1–40%, typically 1–15%, most typically 3–7% solid matter contents. Limitations are mainly due to the pumpability of the fibre suspension in the inlet and outlet tubes.

The adjacent cages, rotors, blades or the like of the flow-through mixer typically move in opposite directions, which enables effective, successive impacts in opposite directions, that is, impacts and counter impacts, to be brought to bear on the fibre suspension flowing through the reactor. If, on the other hand, stationary cages, or stators, are arranged between the cages moving in the same direction, that is, between the rotors, it is possible to bring the impacts produced by the rotor blades and counter impacts caused by the rotor blades colliding with the stator blades to bear on the fibre suspension flowing through the reactor. A similar result can be produced with rotors moving in the same direction at highly different speeds.

The blades or the like of the rotors and stators of the flow-through mixer can also direct the fibre suspension to proceed radially outwards from the cage centres. As the rotor and stator cages increase in size outwards from their centres, a pressure difference is created between the inlet of the flow-through mixer, or the centre, and the outlet, or the outer cage. The pressure drops when moving outwards from the centre. The consequent pressure difference helps the passage of the fibre suspension through the flow-through mixer.

According to a preferred embodiment of the invention, mechanical activation is the case, for example, when the fibre surfaces are treated in a manner that uncovers free and reactive fibre surfaces, to which the precipitating mineral materials can easily adhere, or in such a manner that brings fibrils to the surfaces of the fibres, to which fibrils the precipitating mineral material can easily adhere. The formation of fibrils increases the specific surface area of the fibres, enabling the fibre to bind increasing amounts of precipitating mineral material. Some of the

fibrils formed may be detached from the fibres and thus increase the amount of fines in the fibre suspension, which in some cases is desirable.

According to a preferred embodiment, mechanical activation is also the case when the fibres are treated with over- and under-pressure pulses in such a manner that the fibres open up, tear or so that holes are formed in them, enabling a larger amount of the reactive mineral material in the fibre suspension to penetrate into the fibre and to precipitate there.

According to a preferred embodiment, chemical activation is the case, for example, when the fibre surfaces are activated in such a manner that active chemical groups, which are able to bind precipitating or precipitated mineral material, are formed on the fibre surfaces. For example, active OH-groups, which are able to form bonds with the mineral material and to bind the mineral material to the fibres, can be created on the fibre surfaces.

According to a typical method of this invention, the fibre material and the reactive mineral material, such as milk of lime,  $\text{Ca}(\text{OH})_2$ , are preferably combined in a fibre suspension before introducing these materials into the precipitation reactor. The fibre suspension containing fibre material and reactive mineral material is typically formed by adding the reactive mineral material to be precipitated in the form of a slurry or suspension to the fibre material suspension. The slurry or suspension can be mixed quickly and evenly into the fibre suspension. On the other hand, the reactive mineral material to be precipitated may also be added into the fibre material suspension in solid form, for example, in the form of a powder. When the reactive mineral material is added to the fibre material suspension prior to feeding the suspension into the precipitation reactor, the fibres have several minutes to absorb reactive mineral material, if desired, and in case the mineral material is alkaline, it contributes to swelling the fibres into an advantageous form as regards activation and/or carbonating. In this case, the mineral material is more easily precipitated onto and into the fibres at the

beginning of the precipitation process. If desired, the fibre material and the mineral material may naturally be introduced into the precipitation reactor separately, allowing them to mix only in the precipitation reactor.

When applying the method according to this invention, the mineral material precipitation conditions, such as the raw material, the feed ratio of the raw material, pH, pressure and temperature may be chosen to suit the process in question. The solutions of this patent do not set any limitations to these conditions.

This description refers, unless otherwise mentioned, to

- a fibre material suspension, meaning a liquid based suspension containing at least fibre material,
- a fibre suspension, meaning a liquid based suspension containing at least fibre material and a reactive mineral material necessary for precipitation,
- a gas suspension, meaning a suspension formed of fibre material, a reactive mineral material and a gaseous precipitant, in which the fibre material and the reactive material are fine-grained, and
- the treated fibre suspension, meaning a liquid-based suspension containing at least fibre material and precipitated mineral material particles.

The above-mentioned suspensions may naturally also contain other materials, such as precipitated mineral particles or non-precipitated mineral material.

In accordance with the method of the present invention, the reactive mineral material used may be calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ), that is, milk of lime, or other  $\text{Ca}^{2+}$  ion sources, whereby so-called precipitated calcium carbonate (PCC) can be made to precipitate onto and/or into the fibres. The present invention also enables the use of other similar reactive mineral materials, such as calcium oxide or calcium sulphate, which may be precipitated onto and bound to the fibres with a gaseous precipitant.

The reactive mineral material used in precipitation is chosen according to which property in the fibres, the manufactured paper or the manufacturing process is to be improved. A mineral material being to be precipitated into the fibre suspension, especially into the fibres, can help to enhance paper properties, such as whiteness, brightness, opacity, gloss, bulk, print, printability, drainability, drying, etc.

A gaseous precipitant is preferably used as the precipitating chemical. For example, carbon dioxide can thus be used as a gaseous precipitant for calcium hydroxide. Hence, gas containing carbon dioxide, such as pure or nearly pure carbon dioxide (CO<sub>2</sub>), flue gas or other suitable gas can be fed into the precipitation reactor. Other suitable precipitants besides carbon dioxide may also be used.

The invention makes it possible to precipitate precipitable reactive substances in the fibre suspension not only onto the fibres but also onto the surfaces of other non-organic or organic particles in the suspension. These particles may include, for example, mineral material particles. Such particles may be titanium oxide particles, particles of impurities, or fines from the fibres. The method of the present invention may in this case also be used to cover ink residues left on incompletely de-inked fibres with precipitated calcium carbonate or a corresponding substance. Reactive substances precipitated onto non-organic particles have the capacity to bind the particles to fibres, in which case the particles are retained with the fibres in the paper. On the other hand, the mineral material precipitated onto the fibres has the capacity to bind fibres to each other, which enhances the strength of the paper to be manufactured.

In addition to the fibre material and the reactive mineral material to be precipitated, the fibre suspension fed into the precipitation reactor may contain other solids used in papermaking or the like, such as

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- another mineral material, such as calcium oxide, calcium sulphate, calcium carbonate, talc, kaolin or titanium oxide,
- fibre-based fines, other fines or impurities, such as impurities detached from the fibres during de-inking, various process rejects and/or
- substances used for enhancing retention, such as starch and biocides.

Many of the above-mentioned substances can be introduced into the paper pulp containing PCC after the reactor phase, before the paper pulp is fed from the headbox to the forming section, onto one moving forming base (wire) or between two moving forming bases (wires).

The present invention is suitable for use in the manufacturing of paper, paperboard or other corresponding pulp or web form product made out of fibre-like material. Consequently, the present invention is suitable for use in

- the manufacture of various web form products, such as newsprint, fine paper, magazine paper, kraft paper, tissue paper, special paper or paperboard;
- the manufacture of products made out of various types of pulp, such as chemical, mechanical, chemimechanical, thermomechanical or semimechanical pulp, recycled fibre pulp, or a mixture of these;
- the manufacture of paper made out of various types of fibres, such as primary fibre, chemical or mechanical fibre, bleached or unbleached fibre, ground or non-ground fibre, dried or non-dried, inked or de-inked recycled fibre or fibre obtained from machine broke, or in the manufacture of paper made from a mixture of these.

Paper pulp containing filler (for example PCC) produced in paper manufacture by the method described above is fed at an appropriate consistency from the headbox to the paper machine forming section, which may be a single or twin wire former (one or two moving, forming bases that are permeable to water). In this forming section the coherent, continuous paper web is formed out of the

paper pulp ingredients as water and the materials and any suspended fines dissolved in the water drain through the above-mentioned one or two forming bases. In a preferred embodiment, the production process is a neutral-alkaline paper manufacturing process, which means that the pH of the fibre suspension is generally between 6.5 and 9. The fibre suspension containing PCC obtained by pretreatment can be fed from the reactor to the pulp chest, from where it is passed through backwater dilution (e.g. wire pit) to the pulp processing apparatuses (de-aeration, screens, etc.), which are located before the headbox. Before the headbox, other substances, such as substances that influence the structure of the paper, for example wet end sizing agents (e.g. ASA, AKD), compatible with the neutral alkaline-paper manufacturing process and/or auxiliary agents, for example, retention enhancing agents, can be mixed into the treated fibre suspension containing PCC.

It is also possible that a fibre suspension containing PCC forms a part of the final paper pulp that determines the composition of the paper web, which pulp has been obtained by mixing the above-mentioned treated fibre suspension into one or more other pulp fractions that contain other fibres.

If in pretreating the fibre material of the paper pulp, the fibres and reactive mineral material in the form of a fine fibre suspension are fed into the gaseous precipitant, i.e. in the opposite way to the previous methods, the reactive mineral material, the fibre material and the gaseous precipitant can be mixed together with considerable ease and efficiently in terms of precipitation.

The precipitation reactions can start immediately, and the reactions occur rapidly on the substantially large contact surfaces between the small fibre suspension drops and the gas. Precipitation is easily achieved both onto the surfaces of the fibres as well as into the fibres. By adjusting the composition of the fibre material, the reactive mineral material and/or the gaseous precipitant, the method and

apparatus of the present invention it is possible to control the paper properties that are obtainable, such as strength and optical properties.

It is assumed that the more finely the fibre suspension is dispersed, the faster and more effective the reactions.

A flow-through mixer that operates according to the impact mill principle enables the dispersion of the fibre suspension into a gaseous precipitant to form a mist-like gas suspension, wherein the gas, the fibres, and the reactive mineral material to be precipitated are mixed together extremely efficiently. The method of the present invention enables the components of the precipitation process to be microhomogenised to form a gas suspension wherein the different components may react with each other immediately. This is preferable particularly when, for example, an activated fibre is inclined to return to a non-activated state, that is when the fibrils or holes forming in the fibre are inclined to close. The mineral material in the fibre suspension has at least partially a tendency to prevent the reversion of the fibrils. If required, the fibre suspension may be re-activated once or several times.

By activating the fibre material prior to the precipitation phase and/or during the precipitation phase in a way that enhances the capacity of the fibres to bond with each other and to bind precipitated mineral material, it is possible to obtain a more efficient precipitation phase and improved paper properties. Even a single treatment in the precipitation reactor may suffice to obtain the desired precipitation phase and the desired paper properties.

In the following, a brief description of the invention is given with reference to the accompanying drawings, wherein

**figure 1** illustrates schematically and by way of an example a vertical cross-section of a precipitation reactor in accordance with the method of the present invention;

**figure 2** illustrates schematically and by way of an example a horizontal cross-section of a dispersion and activation phase arranged in a precipitation reactor as shown in figure 1;

**figure 3** illustrates schematically and by way of an example a vertical cross-section of a second precipitation reactor in accordance with the method of the invention;

**figure 4** illustrates schematically and by way of an example a horizontal cross-section of a dispersion and activation apparatus arranged in a precipitation reactor such as the one shown in figure 3;

**figure 5** illustrates schematically and by way of an example a vertical cross-section of a precipitation reactor group in accordance with the method of the invention;

**figure 6** illustrates schematically and by way of an example a vertical cross-section of a second precipitation group in accordance with the method of the invention;

**figure 7** illustrates schematically and by way of an example a vertical cross-section of a third precipitation reactor group in accordance with the method of the invention, and

**figure 8** illustrates schematically a method for manufacturing the paper according to the invention.

Figure 1 illustrates a continuous precipitation reactor 10 in accordance with the invention, which comprises a precipitation vessel 12, dispersion and precipitation apparatus 14 arranged in the precipitation vessel, a fibre suspension inlet tube 16, a gaseous precipitant inlet tube 18 and a treated fibre suspension outlet tube 20. In addition, the apparatus comprises a drive 22 and bearings and sealing 24 between the drive 22 and the apparatus 14.

The dispersion and activation apparatus 14, of which a horizontal cross-section is shown in figure 2, is a so-called flow-through mixer, which has six concentric cages 26, 26', 26", 28, 28', 28" equipped with blades 26a, 26'a, 26"a, 28a, 28'a, 28"a. In apparatus 14, the fibre suspension is dispersed into small particles, liquid drops and/or solid particles. The same apparatus 14 is used to activate the fibres of the fibre suspension in a way that enhances the capacity of the fibres to bond together and to receive precipitated mineral material. The residence time in the dispersion and activation apparatus is short, <10 s., typically <2 s., most typically even less than 1 s.

As the arrows in figure 2 indicate, the first cages 26, 26', 26" of the dispersion apparatus serve as rotors, which in the case shown in the drawing move counterclockwise. The other cages, 28, 28', 28", adjacent to the first cages, also serve as rotors but, in the case shown in the drawing, move clockwise. The cages have been fitted with blades 26a, 26a', 26a", 28a, 28'a, 28a", which collide with the fibre suspension moving radially outwards through the apparatus, subjecting it to repeated impacts and counter-impacts. At the same time, over-pressure forms between the adjacent blades of the rotor as the blades approach each other, and under-pressure is formed as the blades move away from each other. The differences in pressure create very rapid under- and over-pressure pulses. At the same time, shearing forces and turbulences are created in the fibre suspension passing through apparatus 14.

The fibre suspension or fibre slurry containing fibre material and reactive mineral material is fed through tube 16 into the centre 30 of the dispersion and activation apparatus, from where the fibre suspension, induced by the rotor blades and the pressure difference between the centre and outer cage, moves radially outwards towards the open outer edge 32 of the outermost cage 20". If required, the fibre suspension can also be fed into the apparatus 14 between the cages. If desired, the fibre material and the reactive mineral material can be fed into the dispersion

and activation apparatus 14 through separate tubes, in which case the fibre suspension containing fibre and mineral material is not formed until this stage.

The impacts and counter impacts, shearing forces and turbulence as well as the over- and under-pressure pulses caused by the rotor blades moving in opposite directions disperse the fibre suspension into extremely fine parts, liquid drops and solid particles, simultaneously activating the fibres, for example by fibrillation. The activation is effective due, among other things, to the powerful impacts and the great shearing forces exerted on the fibre suspension. In accordance with the method of the present invention, however, the fibre suspension is able to move along a relatively open route through the cages and is therefore not subjected to such grinding and fibre-breaking forces as are fibres processed by disc or cone refiner-type methods. In accordance with the solution of the present invention, the fibres touch the surfaces of the rotor blades only momentarily, if at all.

In the pretreatment phase illustrated in figures 1 and 2, in accordance with the method of the invention, the gaseous precipitant is fed into the centre 30 of the cages of the dispersion and activation apparatus by tube 18. From this central point, the gas flows radially outwards, forming a gas space 34 containing a gaseous precipitant in both the dispersion apparatus and the space surrounding it in the precipitation vessel 12. The gas is discharged from the upper part of the precipitation reactor by tube 21. If desired, the gaseous precipitant may also be fed into and/or between the cages of the dispersion and activation apparatus. The precipitating reactions may already start in the gas space of the dispersion and activation apparatus.

While being treated in the dispersion and activation apparatus 14, the fibre suspension forms extremely fine drops and particles that are dispersed from the apparatus 14 into the part 34' of the gas space surrounding it. The fine drops and particles are flung out of the dispersion and activation apparatus, mainly from the whole area of its outermost cage in a mist-like flow 36. Outside the dispersion

and activation apparatus, the precipitation reactions may continue for a relatively long time, as the fine drops and particles spread out over a large area in the precipitation vessel. The treated fibre suspension settles in a pool located at the bottom of the precipitation vessel and is discharged from the vessel via tube 20.

The size, shape, width and height of the precipitation vessel 12 may be selected so that the drops and particles being flung out of the dispersion and activation apparatus have an optimal residence time in the gas space 34' of the precipitation vessel. The residence time of the fibre suspension can be prolonged, for example, by adding to the height of the precipitation vessel 12, making its shape tower-like.

The processes taking place in the precipitation reactor 10 can also be controlled by adjusting, for example, the number of cages in the dispersion and activation apparatus, the distance between the cages, the distance between the blades on each cage or the blade dimensions and position.

The fibre suspension discharged from the bottom of the precipitation vessel 12 can be circulated back into the same precipitation reactor or fed into another reactor in order to complete the treatment.

In figures 3 and 4, which illustrate another pretreatment phase, the precipitation reactor along with its dispersion and activation apparatus in accordance with the method of the invention, the same reference numbers are used as in figure 1 and 2, where appropriate. The second precipitation reactor 10 in accordance with the present invention shown in figure 3 differs from the ones shown in figures 1 and 2 mainly in that the reactor comprises a dispersion and activation apparatus 14 equipped with an enclosed outermost cage 32 and in that the precipitation reactor does not comprise a separate precipitation space extending beyond the dispersion and activation apparatus. A method in accordance with figures 3 and 4 is suitable for use, for example, when it can be assumed that the precipitation

reactions have time to occur in the desired manner already in the gas space of the dispersion and activation apparatus.

In a dispersion apparatus such as the one in figures 3 and 4, a housing 40 surrounds the outermost cage 28", enclosing the cage. An outlet 42 has been formed in the housing for discharging the treated fibre suspension from the apparatus 14. The treated fibre suspension may be fed through the outlet 42 to further treatment or a further process.

The reactor in figure 3 is suitable for use in activating the fibre suspension also in cases where the precipitation does not take place in this apparatus. Both the precipitation reactor in figure 1 and the reactor in figure 3 may be arranged to form a series of two or more reactors. Figure 5 presents a group of three precipitation reactors such as the one shown in figure 1. In this drawing, the same reference numbers are used as in the previous figures, where appropriate.

Figure 5 presents three precipitation reactors 10, 10' and 10", wherein the fibre suspension containing  $\text{Ca}(\text{OH})_2$  is treated with  $\text{CO}_2$  gas in order to carbonate the  $\text{Ca}^{2+}$  ions, i.e. in order to precipitate the  $\text{CaCO}_3$ . The reactors are connected in series in such a manner that the partly treated fibre suspension containing fibres, precipitated carbonate and unprecipitated calcium hydroxide from the first reactor 10 is fed from outlet 20 to inlet 16' of the second reactor 10'. From the second reactor 10' the treated fibre suspension is respectively fed from outlet 20 to inlet 16" of the third reactor 10".

Carbon dioxide-containing gas is fed into each reactor via tubes 18, 18' and 18". Via inlet 18, carbon dioxide-containing gas is introduced into the first reactor 10, starting the precipitation (carbonating) and the formation of active carbon on the fibres already in the dispersion and activation apparatus 14. The precipitated calcium carbonate precipitates both onto the fibres and onto other particles in the fibre suspension. Carbonate is also precipitated as separate particles into the

fibre suspension. The same or other carbon dioxide-containing gas may be fed by tubes 18' and 18" into the second and third precipitation reactor 10' and 10" in order to complete the precipitation reactions (carbonation). The gas is discharged from the reactors via outlets 21, 21' and 21".

The fibre suspension fed to the precipitation reactor 10 may be activated before feeding it to the reactor in a separate activation apparatus connected before the precipitation reactor 10. The activation apparatus is preferably an impact mill-type flow-through mixer.

Figure 6 presents a second precipitation reactor group, which includes two serially connected precipitation reactors 10 and 10' according to figure 1. Before the first precipitation reactor 10 there is a flow-through mixer-type activation apparatus 44 mainly structured as in figure 3. Inside this activation apparatus the fibre material fed to the precipitation reactor is activated. Gaseous precipitant is not, however, fed into the activation apparatus.

The fibre material is fed via tube 46 to the activation apparatus 44 from above. The activated fibre material is fed through an intermediate tank 48 to the first precipitation reactor 10. A precipitating mineral material, calcium hydroxide, may be added to the suspension via tube 50 before the activation apparatus 44 or via tube 52 after the activation apparatus. In the intermediate tank 48 the fibre suspension is allowed to swell for a predetermined period of time in alkaline conditions. From the intermediate tank, the fibre suspension, including the fibre material and precipitating mineral material, is fed via a tube 16 from below into the dispersion and activation apparatus 14. The gaseous precipitant 18, typically carbon dioxide, is fed along with the fibre suspension into the apparatus 14. Gas is discharged from the upper part of the precipitation reactor via tube 21, the gas typically containing steam and carbon dioxide. The gas is fed for processing in the gas washing and cooling apparatus 54. The carbon dioxide-containing gas processed in the apparatus 54 is circulated via the tube 18 back to the

precipitation reactor 10. The treated fibre suspension collecting in the bottom part of the precipitation reactor is discharged from there into the outlet tube 20.

The second precipitation reactor 10' in figure 6 functions mainly in the same manner as the first precipitation reactor 10. The fibre suspension discharged from the bottom part of the first reactor 10 into tube 20, typically including the fibre suspension, calcium hydroxide and furthermore the precipitated calcium carbonate, is fed via tube 16' from below into the dispersion and activation apparatus 14' of the second reactor 10'. From the washing and cooling apparatus 54, the carbon dioxide-containing gas is led to the second reactor 10'. From the bottom part of the second reactor 10', a fibre suspension which is mainly ready treated and the desired amount of calcium carbonate has typically precipitated onto the fibres, is discharged via tube 20'. From the upper part of the second reactor 10' gas is discharged and taken to the gas washing and cooling machine 54 for recirculating.

Figure 7 presents a third group of precipitation reactors, consisting of three precipitation reactors 10, 10' and 10" connected in series. The reactors are connected one on top of the other, and the fibre suspension is fed into the dispersion and activation apparatus of the reactors from above. The first reactor 10 is on top and the third reactor 10" is at the bottom, so that the fibre suspension flowing through the reactors goes mainly downwards. In front of the third precipitation reactor, a separate preactivation apparatus 44 according to figure 6 and an intermediate tank 48 have been arranged.

The advantages of this invention include the following:

- the fibre suspension may simultaneously be activated and dispersed for the precipitation,
- the precipitation reactions are extremely fast, effective and complete, and good results are achieved even with one run through the precipitation reactor;

- the activation process achieves strong and effective treatment of the fibres without, however, especially breaking or otherwise damaging the fibres;
- the activation process can be regulated;
- extremely effective mixing of the fibre suspension, mineral material and gas is achieved, as a result of which each small volume unit in the fibre suspension is treated, and precipitation takes place in each volume unit;
- precipitation into the fibres can also be influenced;
- the precipitation reactions bond the fibres together, and it may be assumed that the paper strength is improved;
- the precipitation reactions can cover ink residues that are left in the fibres after de-inking;
- the precipitation reactions can bind inorganic and organic particles to the fibres and therefore cause them to be retained in the paper, and
- the precipitation enables qualities such as brightness, strength and opacity of the paper to be optimised better than before;
- pretreatment may be integrated into a continuous papermaking process, where a continuous paper pulp flow is formed from the PCC-containing fibre suspension obtained from pretreatment, which suspension is fed from the headbox to the forming section.

Figure 8 presents schematically a method for papermaking. From the pulp chest M, into which the fibre suspension is fed after the above-described pretreatment process, the fibre material is fed via dilution (e.g. wire pit P) to pulp preparation equipment, and from there the paper pulp is fed to the headbox H and to the forming section F, where the continuously progressing paper web W is formed.

The purpose of the tests presented in the following example is to compare the carbonation of the fibre/PCC product according to this invention with other presented methods. The purpose is to illustrate this invention, not to restrict its scope.

The materials used in all these tests were the same kind of machine-ground pine fibre for fine paper making, the concentration being about 3.5%, Ca(OH)<sub>2</sub> slurry with solid matter about 17%, and a CO<sub>2</sub>-containing gas with a similar composition.

(K1) By a method according to this invention a fibre/PCC fibre product was formed by mixing fibre pulp containing pine fibre and a required amount of Ca(OH)<sub>2</sub> slurry, in order to reach a fibre/PCC ratio of 70/30 after the precipitation, and thereafter pumping the fibre/Ca(OH)<sub>2</sub> suspension twice through the precipitation reactor shown in figure 1. The fibre/Ca(OH)<sub>2</sub> suspension was then pumped according to the method of the invention in the form of a fine suspension into the CO<sub>2</sub>-containing gas. An excess of CO<sub>2</sub>-containing gas was then fed into the apparatus. After this treatment the pH of the fibre/PCC product was 7.

(V1) For comparison a fibre/PCC product was formed with a fluidising chemical mixer by pumping the fibre/Ca(OH)<sub>2</sub> suspension six times through the chemical mixer. Additionally, an excess of CO<sub>2</sub>-containing gas was fed into the chemical mixer. Immediately after the treatment the pH of the fibre/PCC product was 7.

(V2) For another comparison a similar precipitation as in the test (V1) was performed, except that the chemical mixer was not allowed to fluidise, and only an excess of CO<sub>2</sub>-containing gas was fed into the mixer. The fibre/Ca(OH)<sub>2</sub> suspension was pumped eight times through the chemical mixer. Immediately after the treatment, the pH of the fibre/PCC product was 7.

(K1) The pH of the product made according to this invention was 7, even 24 hours from production, which proves that the carbonation was complete.

(V1) The pH of the product made according to this example was 10 after 24 hours from production, which proves that the carbonation was not complete, but the carbonation of the product had to be continued for several minutes in order to

complete the carbonation reactions. Incomplete carbonation causes problems in the chemistry at the wet end of the paper machine during papermaking.

(V2) The pH of the product made according to this example was 11 after 24 hours from production, which proves that the carbonation was not complete, but the carbonation of the product had to be continued for several minutes in order to complete the carbonation reactions.

In all of these tests the time required for the actual carbonation was short, but only with the method of this invention was the carbonation complete in an extremely short time and no further carbonation was required.

It is not the purpose to limit the scope of this invention by the above-described descriptions and examples presented by way of examples, but the purpose is to widely apply this invention within the scope of the patent claims presented below. Therefore the method of this invention can be used in a manufacturing method for paper, paperboard or the like, in any other pretreatment of fibre material used as a raw material in paper, paperboard or the like, in order to activate the fibres and their surfaces, for example, in such a manner that their capacity to bond mechanically or chemically increases, their capacity to bind mineral material mechanically or chemically increases, active OH-groups are formed on their surfaces and/or that their inner parts (lumen) open up allowing, among other things, the mineral material to be precipitated also into the fibres. The fibre material is then pretreated in a flow-through mixer operating by the impact mill principle, which includes

- several, typically 3–8, most typically 4–6, concentric cages provided with blades, from which at least every other cage functions as a rotor, and the cages adjacent to said cages function as stators or rotors, the speed difference of the adjacent cages being 10–500 m/s, preferably 50–200 m/s,
- feeding apparatus for feeding the fibre material mainly into the centre of said cages and

- an open outer cage, which allows the fibre suspension to flow radially outwards through the cages to exit the cage in different directions, or an outer cage provided with one or more outlets in order to discharge the fibre suspension flowing radially outwards from the cages.

The pretreatment is performed preferably when the fibres are swollen, for example, due to the addition of  $\text{Ca}(\text{OH})_2$ . The pretreatment of the fibres according to this invention is especially suitable for activating the fibre material before bringing the fibre material into contact with the reactive mineral material, which mineral material is to be precipitated onto the fibres. The pretreatment according to this invention is, nevertheless, also suitable to be used in other processes in which the aim is to pretreat the fibre material in order to achieve similar properties required in the fibre material.

In a paper made according to this invention the filler PCC is "hidden" inside the fibre mesh and inside the lumens, in such a manner that it does not affect the forming of bonds or sheet formation. This kind of paper has better strength properties than a paper in which the PCC derives from a mineral added to the paper pulp fibres as such.

The 80 g/m<sup>2</sup> paper according to this invention was made with a PCC/fibre ratio of 30/70 and the reference paper was a paper into which the PCC was introduced as a normal additive. The paper made according to this invention had a better tensile strength index (19.3 -> 30.9) and tear resistance index (7.0 -> 9.0). Folding strength increased from 6 to 31.

This paper also has lower porosity (the sheet is denser), and an improved opacity and formation compared to the reference paper. The brightness of the sheet also diminishes compared to a paper that contains the same amount of normal filler, since part of the filler is "hidden".

The fibre in the paper, provided with PCC and pretreated as described above, comprises preferably at least 20 wt-% PCC of the dry weight of the treated fibres, preferably 20–50 wt-%. Preferably the fibre comprises at least 25 wt-% PCC, for example 25 wt-%–50 wt-% introduced onto the fibre in the manner described above. The paper pulp may include other fibres, in which case the proportion of PCC introduced in the above-described method of the paper pulp's total weight diminishes correspondingly. Preferable is a paper product in which all the raw fibre material is pretreated according to the above-described method, in which there is at least 20 wt-% PCC, preferably 20 wt-%–50 wt-%, most preferably at least 25 wt-%, for example 25 wt-%–50 wt-%.

The PCC in the paper made according to the invention, which is introduced onto the fibres by the above described method, is nano-sized precipitated calcium carbonate that typically has a particle size below 100 nm. By selecting the precipitation conditions it is possible to affect the average size of the particles and the size distribution.

It is also possible to supplement the nano-sized filler in the pretreated fibres by adding other fillers. The additional filler may be a normal-sized filler, for example, separately precipitated PCC, or a chemically different filler.

The paper made according to the method of this invention may be finished after the drying of the paper web on the paper machine either on-line or as a separate finishing process. In order to finish the surface, the paper web may, for example, be calendered. A paper web made according to the above-described method may be used, after the possible calendaring, as such as printing paper (e.g. SC paper), or the paper web may, after the possible calendering, be coated on-line or in a separate coating machine (e.g. LWC paper), in which case the coating functions as a printing surface. If the fibre material onto which the PCC is introduced in the pretreatment is a chemical pulp, the printing paper product formed mainly or solely from this pulp may be an uncoated fine paper, i.e. WFU,

or a coated fine paper, i.e. WFC, or a copying paper. This invention is nevertheless not restricted to printing papers, but can be applied to all paper products. In the patent claims the term "paper" refers to all resilient, fibre based products originally made in the form of a web, regardless their grammage, including paperboard.